

AMENDED SPECIFICATION

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NO DRAWINGS

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COMPLETE SPECIFICATION

Improvements in the Production of Condensation Products

We, BADISCHE ANALIN- & SODA-FABRIK AKTIENGESELLSCHAFT, a Joint Stock Company organised under the laws of Germany, of Ludwigshafen on Rhine, Germany, do hereby
5 declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to the production of condensation products from copolymers of alpha, beta-ethylenically unsaturated alpha- or beta-substituted monocarboxylic acid amides, formaldehyde and alcohols, wherein
15 said copolymers are free from amides of acrylic acid.

It is already known to react acrylamide or methacrylamide with formaldehyde and to
20 polymerize the resultant methylol compounds of unsaturated amides. Polyacrylamide and polymethacrylamide have also already been condensed in aqueous or organic solution with formaldehyde. In both cases strongly cross-linked products are obtained which are in-
25 soluble in organic solvents and are only swellable in water. Their practical use is therefore limited.

It is furthermore known to mix copolymers of unsaturated carboxylic acid amides with
30 paraformaldehyde and to use them for the production of coatings after the addition of hardening agents. For example copolymers of methacrylamide and acrylic esters have already been prepared in the form of bead polymers
35 in water, then dissolved in organic solvents and these solutions finally mixed with paraformaldehyde or formaldehyde condensates of urea or melamine. Films and coatings prepared therefrom soften in boiling water and
40 become milky turbid. Furthermore they are not fast to rubbing, become cloudy in organic solvents at the boiling temperature, swell strongly therein and even partly dissolve.

Copolymers of unsaturated carboxylic acid amides which are prepared in alcohols or ketones as solvents, can be treated in the same way. The amide groups of the copolymer
45 thereby do not react completely with formaldehyde so that a great part of the formaldehyde is lost in the hardening process. The process is thus not economical and moreover
50 leads to troublesome odours. The films obtained are opalescent, tend to sweat and are sensitive to water and organic solvents.

British Patent Specification No. 467,492
55 describes the condensation of amides of unsaturated carboxylic acids, or their polymers and copolymers, with formaldehyde. This condensation reaction can be carried out in the presence of alcohols, alcohol mixtures
60 and/or metal compounds. Under the reaction conditions described, however, no etherification of the methylol compounds with the alcohols used will take place because the reaction is carried out in a neutral or basic
65 medium and not in the presence of etherification catalysts.

We have now found that the said disadvantages can be obviated by etherifying a copolymer reacted with formaldehyde from one or
70 more primary amides of alpha-beta-ethylenically unsaturated alpha- or beta-substituted monocarboxylic acids and/or one or more primary amides of alpha,beta-ethylenically
75 unsaturated dicarboxylic acids and one or more other ethylenically-unsaturated polymerizable compounds with the exception of amides of acrylic acid in the presence of etherification catalysts, said copolymer being soluble in an
80 organic solvent consisting of or containing a monohydric alcohol free from aliphatic unsaturation, said etherification being effected during or after the conversion of the copolymer with formaldehyde. Alpha,beta-ethylenically
85 unsaturated alpha- or beta-substituted monocarboxylic acid amides which may be con-

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tained in the said copolymers are preferably the alpha- or beta-homologues of acrylamide such as methacrylamide, alpha,ethylacrylamide or crotonamide; suitable alpha,beta-ethylenically-unsaturated dicarboxylic acid amides are especially alpha,beta-ethylenically-unsaturated alpha,beta-dicarboxylic acid diamides, such as fumaric acid diamide or maleic acid diamide. According to this invention amides of carboxylic acids with up to about 8 carbon atoms and preferably with up to 5 carbon atoms are especially useful.

Other ethylenically-unsaturated copolymerizable compounds are for example singly or multiply ethylenically-unsaturated hydrocarbons with up to about 8 to 10 and preferably up to 6 carbon atoms such as butadiene, isoprene, isobutylene or vinyl compounds, especially vinylaromatic compounds, as for example styrene or its alkyl derivatives, but preferably acrylic compounds, such as esters of acrylic or methacrylic acid, or a alpha-ethylacrylic acid, crotonic acid, maleic acid or fumaric acid, with monohydric aliphatic alcohols, preferably saturated, which may be primary, secondary or tertiary and may have branched or unbranched chains. These alcohols, with which the acrylic acids or in general alpha,beta-ethylenically-unsaturated mono- or di-carboxylic acids are esterified, may contain less than 5 carbon atoms. Products having quite specially good properties are obtained, however, by subjecting to etherification during or after their conversion with formaldehyde, those copolymers which have been prepared from alpha,beta-ethylenically-unsaturated alpha- or beta-substituted mono-carboxylic acid amides and/or alpha,beta-ethylenically unsaturated dicarboxylic acid amides and esters of alpha,beta-ethylenically-unsaturated carboxylic acids with aliphatic, preferably monohydric, alcohols with more than 5 and up to about 20, especially to about 12 carbon atoms. The carbon atoms of the aliphatic alcohols used for esterification of the alpha,beta-ethylenically-unsaturated carboxylic acids may also be wholly or partly arranged in a cyclic manner. Besides the hydroxyl groups they may also contain other substituents, as for example halogen atoms, aryl radicals or ester groups. Examples of suitable alcohols are methanol, ethanol, propanol, butanol, amyl alcohol, hexyl alcohol as well as cyclohexanol and their alkyl derivatives and aromatic-aliphatic alcohols, such as benzyl alcohol, and especially 2-ethylhexyl alcohol, octyl alcohol, isononyl alcohol, decyl alcohol and dodecyl alcohol.

Furthermore as ethylenically-unsaturated copolymerizable compounds there may also be used vinyl compounds, as for example vinyl esters, preferably of saturated aliphatic mono-carboxylic acids with up to about 4 carbon atoms, as for example vinyl acetate, vinyl propionate, but also vinyl benzoate and also

mono-N- or di-N-substituted amides of unsaturated carboxylic acids with the exception of amides of acrylic acid, especially N-isopropylmethacrylamide and the like, thus preferably mono- or di-N-substituted amides of unsaturated carboxylic acids with the exception of acrylic acid in which the substituents are preferably saturated alkyl radicals with up to about 4 carbon atoms. Furthermore as copolymerizable compounds there may be used vinyl halides, especially vinyl chloride, and also vinylidene chloride, N-vinyl compounds in which the nitrogen atom is a constituent of a saturated or unsaturated cyclic radical, for example N-vinylaromatics, such as N-vinylcarbazole, N-vinyl pyridine and also N-vinylpyrrolidone. Unsaturated polymerizable, especially alpha,beta-ethylenically-unsaturated; mono, and di-carboxylic acids, for example acrylic acid, methacrylic acid, crotonic acid, maleic or fumaric acid, are also suitable.

In general it is necessary that the copolymers should contain about 5 to 50% of an alpha,beta-ethylenically-unsaturated alpha- or beta-substituted mono-carboxylic acid amide or an alpha,beta-ethylenically unsaturated dicarboxylic acid amide in order that the typically good properties of the proposed condensation products should be evident, but they may also contain still larger amounts of carboxylic acid amide. The solubility stated as the criterion for the usefulness of the copolymers used relates to their solubility in the various alcohols which come into question for the etherification of their methylol compounds. Among these may be mentioned all saturated aliphatic unbranched and branched monohydric alcohols, preferably those with up to 18 carbon atoms and especially with about 2 to 12 carbon atoms, for example ethanol, normal-propanol, normal-butanol, iso-butanol, amyl alcohol, hexanol, octanol, 2-ethylhexanol, isononyl alcohol, decyl alcohol and lauryl alcohol. In many cases cycloaliphatic and aliphatic-aromatic alcohols are also suitable, for example cyclohexanol, methylcyclohexanol and benzyl alcohol and also mixtures of alcohols. It is often especially favourable to use these alcohols in admixture with indifferent organic solvents. Such solvents are for example aliphatic, cycloaliphatic or aromatic hydrocarbons, for example benzene, toluene xylene, hexane, octane, gasoline, petroleum ethers or cyclohexane. In general about 5 to 50% of an indifferent organic solvent are used with reference to the total solvent. Larger or smaller amounts of such a solvent may however be used. The alcohol content of the solvent mixture should at least not lie below the amount stoichiometrically necessary for the etherification. The copolymers used must also be soluble in such solvent mixtures.

Mixtures of different alpha,beta-ethylenically unsaturated alpha- or beta-substituted monocarboxylic acid amides and/or alpha,beta-

- ethylenically unsaturated di-carboxylic acid amides and different unsaturated copolymerizable compounds may also be used. For example if a copolymer from such a carboxylic acid amide which has been copolymerized with about 50 to 95% of an ester of an alpha,beta-ethylenically-unsaturated carboxylic acid with an alcohol with more than 3 carbon atoms is used, up to about 75% of the said ester and preferably about 10 to 40% may be replaced for example by a vinyl compound or an acrylic compound. The production of the copolymers takes place by known polymerization methods in solution, block or emulsion and is not claimed in the present application.
- It is frequently advantageous to carry out the polymerization in the presence of the alcohol which is later to serve for the etherification. The condensation of the copolymer with formaldehyde and the simultaneous or subsequent etherification with alcohols is carried out in solution in the alcohols serving for the etherification or in solutions which contain these alcohols. The formaldehyde is preferably used as concentrated, especially up to 40%, aqueous solution, but may also be led in as gas or added as polymeric formaldehyde, for example paraformaldehyde. In general there is used at least 0.75 mol of formaldehyde for each carboxylic acid amide nitrogen atom contained in the copolymer, and preferably 1 to 2 mols of formaldehyde. It is essential to carry out the etherification reaction in the presence of etherification catalysts. Among these may be mentioned all compounds with which a pH value between about 2.5 and 4.5 can be set up, for example inorganic acids, such as phosphoric acid or hydrochloric acid, organic acids, as for example phthalic acid or formic acid, and also compounds which yield hydrogen ions under the reaction conditions, as for example a mixture of glycerine and boric acid or salts of strong acids with weak bases, for example ammonium salts of inorganic acids, and in general compounds which are conventionally used in etherification reactions of aliphatic hydroxyl groups. It is possible first to condense the copolymer with formaldehyde in a non-alcoholic solvent and then to effect the etherification. Non-alcoholic solvents are for example aliphatic or aromatic hydrocarbons, such as butane, hexane, octane, gasoline fractions, cyclohexane, benzene, toluene or xylene or esters, such as ethyl acetate, butyl acetate, amyl acetate, glycol diacetate or ketones, for example acetone, methyl ethyl ketone, cyclohexanone or ethers, such as tetrahydrofuran, di-isopropyl ether, dioxane; or halogen hydrocarbons, as for example chloroform or trichloroethylene. It is presupposed that the copolymers, after the etherification, shall be soluble to the extent of at least 5% in organic solvents. It is especially preferable however to mix the formaldehyde, preferably in concentrated aqueous solution, with the alcoholic or alcohol-containing solution of the copolymer containing amide groups. Especially the solutions of etherified products which contain acrylic acid esters of higher alcohols do not tend to gelatinize prematurely. Their stability makes it possible to prepare solutions with a solids content of, for example, 55% or more while at the same time being of low viscosity, this being important for use as spraying lacquers.
- The power for binding pigments is excellent. The alcoholic solutions, for example the butanol solutions, of the proposed condensates may be diluted well with other lacquer solvents, such as aliphatic and aromatic hydrocarbons. This is of special importance in the combination thereof with other lacquer raw materials, as for example alkyd resins, nitrocellulose, urea resins, melamine resins, urethane resins or phenol resins, with which the proposed condensation products are very well compatible.
- With the condensate solutions obtained it is possible to prepare films and coatings which are very stable to water and many organic solvents even at the boiling temperature, especially when acid hardening agents are added to the condensate solutions. Examples of hardening agents are organic or inorganic acids or acid halides, such as maleic acid, para-toluene sulphonie acid, para-toluene sulphonie acid chloride, hydrochloric acid or nitric acid or acid salts, for example ammonium nitrate. For example a copolymer of 80 parts of butyl acrylate and 20 parts of methacrylamide which has been condensed with formaldehyde and etherified with butanol and to which ammonium nitrate has been added as a hardener, gives, after heating for a short time, for example for 3 minutes at 130°C, a completely transparent film which is stable to light and stable in shape, which has great surface hardness and high surface gloss, and has good flexibility, which does not become sticky even at temperatures above 150°C and remains flexible even at low temperatures. In contrast, the same copolymer, mixed by known methods with paraformaldehyde, gives under the same conditions a matt film which tends to sweat. The condensate solutions obtained according to this invention can be used for the production of coatings on textiles, wood, paper, leather and metals, for example wires, for the production of foils and films, as adhesives for a great variety of materials, as binding agents for pigments, for the production of fibre fleeces and covering coatings on sticky substrates, for example in the production of synthetic leather, and also for impregnations. For these purposes they may be used in admixture with natural or synthetic high molecular weight substances, as for example urea, melamine or phenol resins, alkyd resins, polyamides, poly-

merization products or modified cellulose products.

The products prepared according to this invention from copolymer of alpha,beta-ethylenically-unsaturated alpha- or beta-substituted mono-carboxylic acid amides and/or alpha,beta-ethylenically unsaturated dicarboxylic acid amides and esters of alpha,beta-ethylenically-unsaturated carboxylic acids with alcohols having at least 6 carbon atoms are especially valuable. By hardening carried out with the usual hardening agents at high temperature, they yield flexible and yet very hard products, for example glossy and waterproof coatings, foils and films, stuck products and impregnations.

The following Examples will further illustrate this invention but the invention is not restricted to these Examples. The parts specified are parts by weight.

EXAMPLE 1

1,220 parts of normal butanol, 145 parts of a 32% aqueous formaldehyde solution and 3.5 parts of 81% phosphoric acid are added to a 50% highly viscous solution in 500 parts of normal butanol of a copolymer having the K-value 36.5 which has been prepared in known manner by polymerization of 100 parts of methacrylamide and 400 parts of butyl acrylate with 1.25 parts of azo-bis-isobutyronitrile. Then for 2½ hours from a temperature of 94°C, water and butanol are distilled off azeotropically, the butanol freed from water being continuously returned. After a boiling temperature of 116° to 117°C has been reached, i.e. the boiling point of normal-butanol, the reaction is completed. Then 22.5 parts of 4-normal caustic soda solution are added to the solution and the whole filtered.

EXAMPLE 2

A 50% gelatinous mass obtained from 60 parts of methacrylamide, 90 parts of vinyl propionate, 150 parts of butyl acrylate and 0.75 parts of azo-bis-isobutyronitrile in 300 parts of normal butanol is dissolved in 720 parts of butanol and then 115 parts of 32% formaldehyde and 1.6 parts of 81% phosphoric acid are added. Then water and butanol are distilled off azeotropically for 2½ hours beginning at 94°C, the butanol being continually returned after separation of the water. After a boiling temperature of 116°C has been reached, 13 parts of 4-normal caustic soda solution are added and the product filtered.

EXAMPLE 3

240 parts of butanol, 32 parts of 32% formaldehyde and 0.5 part of 81% phosphoric acid are added to a 50% viscous solution of a copolymer of 5 parts of methacrylamide and 95 parts of butyl acrylate of the K-value 38.5 in 100 parts of butanol. Then water and butanol are distilled off azeotropically for 2½ hours. The butanol is continually returned after the water has been separated. When a boiling temperature of 116°C has been

reached, the reaction has ended, 7 parts of 2-normal caustic soda solution are added to the solution and the product filtered. A clear condensate solution is obtained.

EXAMPLE 4

115 parts of butanol, 23 parts of a 36% formaldehyde solution and 0.6 part of 81% phosphoric acid are added to a 50% gelatinous copolymer of the K-value 17.5 which has been prepared by polymerization of 20 parts of methacrylamide and 80 parts of styrene with an addition of 1 part of benzoyl peroxide and 1 part of ditertiary butyl peroxide in 100 parts of ethylbenzene. This mixture is heated to 90°C and then water and solvent are distilled off azeotropically for an hour. The solvent mixture freed from water is continually returned. After a boiling temperature of 120°C has been reached, the reaction has ended. Finally 5 parts of 2-normal caustic soda solution are added to the resultant solution of the formaldehyde condensate etherified with butanol and the whole filtered.

EXAMPLE 5

155 parts of cyclohexanol, 23 parts of a 36% formaldehyde solution and 0.6 part of 81% phosphoric acid are added to a 50% gelatinous copolymer of the K-value 17.5 which has been prepared by polymerization of 20 parts of methacrylamide and 80 parts of styrene with the addition of 1 part of benzoyl peroxide and 1 part of ditertiary butyl peroxide in 100 parts of ethylbenzene. After heating the mixture to 100°C, 18.5 parts of water are distilled off during 45 minutes, the solvent mixture distilled over being continually returned. After attaining a boiling temperature of 142°C, the reaction is complete. The solution is treated with 5 parts of 2-normal caustic soda solution and then filtered.

EXAMPLE 6

165 parts of benzyl alcohol, 23 parts of a 36% formaldehyde solution and 0.6 part of 81% phosphoric acid are added to a 50% gelatinous copolymer of the K-value 17.5 which has been obtained by polymerization of 20 parts of methacrylamide and 80 parts of styrene with the addition of 1 part of benzoyl peroxide in 100 parts of ethylbenzene. The mixture is heated to 100°C. During 45 minutes, 8.5 parts of water are distilled off, the solvent mixture passing over being continually returned. After reaching a boiling temperature of 150° to 152°C, the reaction has ended, 5 parts of 2-normal caustic soda solution are added to the solution which is then filtered.

EXAMPLE 7

172 parts of a 37% aqueous formaldehyde solution are added to 1,100 parts of the solution of a copolymer which has been prepared by heating for 5 hours a mixture of 150 parts of methacrylamide, 350 parts of acrylic acid 2-ethylhexyl ester, 500 parts of butanol, 100

parts of xylene, 5 parts of dilauroyl peroxide and 5 parts of tertiary butyl perbenzoate at 115°C, and the mixture is heated. When the temperature of the solution is 80°C, 1.1 parts of 81% phosphoric acid are added. The whole is then heated to the boiling point and water and butanol are distilled off azeotropically from 92°C. The butanol freed from water is continuously returned. After about 3 to 4 hours, an internal temperature of 118° to 120°C has been reached and the reaction has ended. 11 parts of 10% caustic soda solution are added and the water again distilled off. The resin solution is finally filtered. A film prepared from this resin solution by casting, after hardening with acid catalysts at elevated temperature, is very glossy, hard and waterproof.

EXAMPLE 8

172 parts of a 37% aqueous formaldehyde solution and 1.1 parts of 81% phosphoric acid are added to 1,100 parts of a solution of a copolymer of 150 parts of methacrylamide and 350 parts of decyl acrylate in 500 parts of butanol and 100 parts of xylene. Water and butanol distilled off azeotropically from this solution and the butanol distilled off is continuously replaced. When the temperature of the solution amounts to 118° to 120°C, 11 parts of 10% caustic soda solution are added, water is again separated and the whole finally filtered. The resin obtained has good compatibility with other lacquer resins, for example with alkyd resins, nitrocellulose, urea resins, phenol resins and urethane resins and also with lacquer solvents.

EXAMPLE 9

14.2 parts of a 37% aqueous formaldehyde solution and 0.1 part of 81% phosphoric acid are added to 100 parts of a 45% solution of a copolymer of 20 parts of methacrylamide, 5 parts of fumaric acid diamide and 75 parts of methacrylic acid 2-ethylhexyl ester in normal butanol. Water and butanol are distilled off azeotropically. When the temperature in the solution amount to 115° to 118°C, 1 part of 10% caustic soda solution is added. After again separating the water, the resin solution is filtered while still hot. Coatings prepared from the resultant resin solution which has been pigmented and to which phosphoric acid has been added are very glossy and waterproof.

EXAMPLE 10

172 parts of a 37% aqueous formaldehyde solution are added to 1,100 parts of a solution of a copolymer of 160 parts of methacrylamide, 200 parts of acrylic acid 2-ethylhexyl ester and 150 parts of normal butyl acrylate in 500 parts of normal butanol and 100 parts of xylene and the mixture is heated. At 80°C internal temperature, 1.1 parts of 81% phosphoric acid are added. Then the whole is heated to the boiling point and butanol and water are distilled off azeotropically

ally in 3 to 4 hours, beginning at 92°C. When an internal temperature of 118° to 120°C has been reached, the reaction has ended. Neutralization is effected with 11 parts of a 10% aqueous sodium hydroxide solution, water is separated and the solution filtered. An about 55% clear solution is obtained which yields flexible and extremely waterproof coatings.

We are aware of Patent No. 826,652 which describes and claims a method of preparing a resinous material which comprises condensing a monoaldehyde with a substantially water-insoluble interpolymer containing an acrylamide in an amount of at least 5 per cent by weight, the monoaldehyde being utilized in an amount of from 0.2 to 3.0 equivalents for each amide group in the interpolymer, the condensation being conducted in the presence of an alkanol containing from one to six carbon atoms under etherification conditions such that the resulting resinous material has at least some amino hydrogen atoms replaced by $-ROR^1$ groups, said R and R^1 groups being alkylene and alkyl groups corresponding to those of the monoaldehyde and alkanol, respectively.

WHAT WE CLAIM IS:—

1. A process for the production of condensation products, which comprises etherifying a copolymer derived from at least one primary alpha,beta-ethylenically-unsaturated alpha- or beta-substituted mono-carboxylic acid amide and/or at least one primary alpha,beta-ethylenically unsaturated dicarboxylic acid amide and at least one other ethylenically-unsaturated polymerizable compound with exception of amides of acrylic acid, in the presence of an etherification catalyst, said copolymer having been condensed with formaldehyde and being dissolved in an organic solvent consisting of or containing at least one monohydric alcohol free from aliphatic unsaturation, and reacting said copolymer with said alcohol contained in the organic solvent.

2. A process as claimed in claim 1 wherein the condensation of the copolymer with formaldehyde and the etherification are carried out in a single step.

3. A process as claimed in claim 1 wherein the etherification of the copolymer is carried out after its reaction with formaldehyde.

4. A process as claimed in any of claims 1 to 3 wherein the copolymer comprises an amide of an alpha,beta-ethylenically-unsaturated alpha- or beta-substituted mono-carboxylic acid and an acrylic compound with exception of acrylamides.

5. A process as claimed in any of claims 1 to 4 wherein the copolymer comprises an amide of an alpha,beta-ethylenically-unsaturated alpha- or beta-substituted mono-carboxylic acid and/or of an alpha,beta-ethylenically unsaturated dicarboxylic acid and an ester of acrylic acid.

6. A process as claimed in any of claims 1 to 5 wherein the copolymer comprises an amide of an alpha,beta-ethylenically-unsaturated alpha- or beta-substituted mono-carboxylic acid and/or of an alpha,beta ethylenically unsaturated dicarboxylic acid and an ester of acrylic acid with an alcohol containing more than 5 carbon atoms.
7. A process as claimed in any of claims 1 to 6 wherein the copolymer comprises an amide of an alpha,beta-ethylenically-unsaturated alpha- or beta-substituted mono-carboxylic acid and/or of an alpha,beta-ethylenically unsaturated dicarboxylic acid and an ester of acrylic acid with a monohydric aliphatic alcohol having more than 5 carbon atoms.
8. A process as claimed in any of claims 1 to 7 wherein the copolymer contains from 5 to 50% of an amide of an alpha,beta-ethylenically-unsaturated alpha- or beta-substituted mono-carboxylic acid and/or of an alpha,beta ethylenically dicarboxylic acid.
9. A process as claimed in any of claims 1 to 8 wherein the copolymer is condensed with such an amount of formaldehyde that there is at least 0.75 mol of formaldehyde for each carboxylic acid amide nitrogen atom contained in the copolymer.
10. A process as claimed in any of claims 1 to 9 wherein the copolymer is condensed with such an amount of formaldehyde that there are 0.75 to 2 mols of formaldehyde for each carboxylic acid amide nitrogen atom present in the copolymer.
11. The process for the production of condensation products substantially as described in any of the foregoing Examples.
12. Condensation products when obtained by the process claimed in any of claims 1 to 11.
13. Any lacquer, coating agent or impregnating agent containing a condensation product as claimed in claim 12.
14. Any film or coating prepared from a condensation product as claimed in claim 12.
15. Any article bonded by means of a condensation product as claimed in claim 12.
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